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# NATURE AND PROPERTIES OF ACID SULPHATE SOILS IN DRAINED COASTAL LOWLANDS IN NEW SOUTH WALES

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## ABSTRACT

Acid sulphate soils pose severe constraints to the protection of engineering infrastructure, sustainable agriculture and environmental quality in coastal estuarine systems in many parts of Australia. The nature and properties of acid sulphate soils are described with reference to data collected from intensively drained coastal lowlands located on the South Coast of NSW. Deep flood mitigation drains are shown to profoundly influence the elevation of the shallow groundwater aquifer, which in turn determines the rate of acid generation from the oxidation of pyrite in the acid sulphate soil layer. Numerical modeling is also used to demonstrate the nature of acid generation in acid sulphate soils. Application of SMASS showed that approximately 1.3 tonnes  $H_2SO_4$  ha<sup>-1</sup> was generated by the oxidation of pyrite during the summer of 1997-98. Extremely acidic groundwater (pH 2-3) was measured after the groundwater rose through the oxidised zone during drought breaking rainfall. Management of the groundwater elevation is shown to be the key for minimising acid generation and transport in drained sub-catchments. Strategies including the construction of weirs in flood mitigation drains, increased irrigation and re-designing floodplain drainage schemes are suggested as offering potential for managing acid sulphate soil under various circumstances.

## 1 INTRODUCTION

The breaking of a prolonged drought in the mid 1980's resulted in severe acidification of many estuaries and rivers in coastal New South Wales. Some rivers had pH<5 for many months. After considerable community outcry and conflict between various industry sectors, acid sulphate soils were 'rediscovered' and shown to be the source of estuarine acidification. Walker (1972) gave ample warning that disturbance of acid sulphate soils by drainage, excavation or aggressive cropping practices may lead to the generation and discharge of acidic products from these soils. Unfortunately, his warnings were largely ignored by governments, industry and the community until the late 1980's.

### 1.1 WHAT ARE ACID SULPHATE SOILS?

Acid sulphate soil is the common name given to coastal floodplain soil and sediment containing oxidisable, or already oxidised, sulphide minerals. The usual form of these sulphides is cubic iron pyrite ( $FeS_2$ ) although other forms of sulphide compounds such as iron monosulphide ( $FeS$ ), greigite ( $Fe_3S_4$ ) and various organic sulphides can also exist in small concentrations (Bush and Sullivan, 1996). Where acid sulphate soils remain in a reduced condition, the sulphides remain chemically inert. These soils are called potential acid sulphate soils. On exposure to the oxygen in air, oxidation of the sulphides takes place. The oxidation reaction generates acidic products, hence the term actual acid sulphate soils. In many instances, oxidising conditions overlie reducing conditions in a soil profile so that actual and potential acid sulphate soils exist in the same soil profile. The term acid sulphate soils refers to the whole soils profile regardless of its oxidation/reduction status. White *et al.* (1997) suggest that the term acid sulphate soil should be used to convey the notion that these soils can pose a significant threat to the integrity of the environment and should be handled with caution.

### 1.2 DISTRIBUTION OF ACID SULPHATE SOILS

The area of acid sulphate soils deposited during the Holocene epoch occupies between  $10^7$ - $10^8$  ha throughout the world (Brinkman, 1982). The world wide distribution of acid sulphate soils is shown in Table 1. The conditions suitable for the formation of pyrite in sediments lend useful clues to the location of acid sulphate soils in the coastal zone (Naylor *et al.*, 1995). Acid sulphate soils occur in wave protected mangroves and marshes, outer barrier tidal lakes and backswamps areas where the accumulation of organic matter and reduced sediments can occur. It is important to recognise that acid sulphate soils also exist in relics of these environments.

Region	Area of ASS (x 10 <sup>6</sup> ha)
Africa	3.7
Asia	6.7
Latin America	2.1
Australia	3.0*

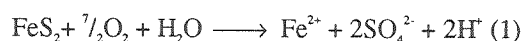
\* estimated by White *et al.* (1997)

**Table 1** World wide distribution of acid sulphate soils

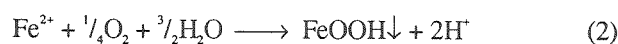
The surface of the sulfuric horizon should be close to the elevation of mean sea level when the acid sulphate soil was being formed. In eastern Australia, this is about 1m above the current mean sea level or 1m Australian Height Datum [AHD]. The acid sulphate soil may have been buried by a variable thickness of alluvial or peat soil, usually to a depth of less than 10m. It is therefore a reasonable assumption to preclude the presence of acid sulphate soils from coastal land at elevations in excess of 10m AHD. Naylor *et al.* (1995) have mapped landform elements likely to contain acid sulphate soils for the coast of New South Wales (approximately 1500km in length). These maps show that New South Wales has 0.4-0.6 x 10<sup>6</sup> ha of acid sulphate soils. White *et al.* (1997) suggest that acid sulphate soils are likely to occur through extensive areas of Queensland, the Northern Territory and Western Australia.

### 1.3 PROPERTIES OF ACID SULPHATE SOILS

Pyrite in moist acid sulphate soils will oxidise when its is exposed to oxygen causing the formation of acidic oxidation products. As the soil pH falls below 4, oxidation occurs rapidly through a temperature dependant, bacteria catalysed reaction. The oxidation reaction involves the conversion of solid pyrite to dissolved iron and sulphate through a series of complex oxidation steps (Willett *et al.*, 1992). This reaction can be summarised as:



Under acidic conditions, Fe<sup>2+</sup> liberated in equation (1) is soluble and can be transported into streams at a considerable distance from the source of pyrite (Ngyuyen and Wilander, 1995). In the stream, Fe<sup>2+</sup> oxidises to produce ferrichydrite (FeOOH), the characteristic red-brown floc, and a further 2 moles of acid. This reaction can be described by:



Iron flocs contribute to environmental and infrastructure damage by smothering benthos (Sammur *et al.*, 1996) and clogging bores and filters. The Fe<sup>2+</sup> oxidation reaction consumes oxygen from the water column and can be associated with low dissolved oxygen concentrations in streams.

The overall reaction for the complete oxidation of pyrite in moist sediments has been described by Dent (1986) as:



For each mole of pyrite that is oxidised, four moles of acid are produced.

Clay minerals can dissolve under strong acidic conditions to release silica and metal ions. Nriagu (1978) shows that the hydrolysis of the common estuarine clay illite under acidic conditions liberates soluble aluminium, iron, potassium, sodium and magnesium. van Breeman (1973) and Willett *et al.* (1992) show that manganese and trace heavy metals can also be released. Blunden *et al.* (1997), Sammur *et al.* (1996) and many others report that the concentration of dissolved metals, particularly aluminium and iron, is logarithmically proportional to the soil solution and/or groundwater pH. Sammur *et al.* (1995) report that dissolved species of monomeric aluminium and iron contribute to the injury and death of fish and crustaceans. ANZECC (1992) recommends that aluminium concentrations should be less than 5µg L<sup>-1</sup> when the pH<6.5 to ensure ecosystem protection. Sammur *et al.* (1996); Indraratna and Blunden (1997) and many others have reported dissolved aluminium concentrations up to three orders of magnitude in excess of these guidelines in surface and groundwater discharged from oxidising acid sulphate soils.

Acid sulphate soils can be encountered during many activities that disturb the soil and/or groundwater in the coastal zone. To better assess and manage acid sulphate soils, the NSW Environment Protection Authority (1995) and the NSW Acid Sulphate Soils Management Advisory Committee (1998) have published a suite of planning, assessment and management, and laboratory testing guidelines to assist proponents of coastal developments minimise the risks

associated with acid sulphate soils. The reader is referred to these documents for further information related to acid sulphate soils for new developments.

However, the legacy of previously constructed drainage works which discharge large quantities of acid into coastal waterways remains a major environmental, economic and social problem that requires urgent attention. Numerous authors (eg, Sammut *et al.* 1996; Blunden *et al.* 1997) have estimated acid discharge rates for drained agricultural land to be in the order of 100-500 kg H<sub>2</sub>SO<sub>4</sub> ha<sup>-1</sup> year<sup>-1</sup>. To gauge an appreciation of the magnitude of the amount of acid generated and discharged by acid sulphate soil areas, Sammut *et al.* (1996) reported that approximately 950t of sulfuric acid, 490t of monomeric aluminium and 97t of dissolved iron were discharged into the Richmond River from the 3000ha Tuckean Swamp during a flood event in 1994. This event resulted in about 90km of the Richmond River becoming acidified at pH<5.

Drainage of coastal lowlands is the major contributing factor to the generation and discharge of acidic oxidation products from acid sulphate soils. The generation and transport of acid produced from the oxidation of pyrite in sulphidic sediments is largely determined by the shallow groundwater hydrology of the catchment. Where groundwater falls below the elevation of the acid sulphate soil horizon, atmospheric oxygen is able to diffuse through the overlying soil layers to react with the sulphide minerals in the acid sulphate soils to generate acid according to the reactions described above. In this sense, appropriate manipulation of groundwater is the key to minimising the generation of acidic oxidation products.

A simplified representation of the water balance of a coastal floodplain may be described by (White *et al.* 1997):

$$P + I + L_i = E_t + R + L_o + D + \Delta S \quad (4)$$

where P is precipitation, I is irrigation,  $L_i$  is the lateral inflow of water,  $E_t$  is evapotranspiration, R is surface runoff, D is drainage to the water table,  $\Delta S$  is change in soil moisture content above the water table, and  $L_o$  is the lateral outflow.

Using the model described in (4), a simple assessment of the implications of land and water management in areas of acid sulphate soils can be undertaken. Acid sulphate soils occur in coastal floodplains where  $P > E_t$ . R and  $L_o$  can be large components of the water balance, resulting in the inundation of low lying backswamps for considerable periods of time. In order to use such low lying areas for agricultural purposes, extensive drainage networks have been constructed to efficiently remove water. One-way floodgates have been installed where drainage systems discharge into tidal systems at low tide to protect against inundation and to drain the land as quickly as possible. A schematic of a typical floodgated coastal drainage system is shown in Figure 1.

Channelised, high density drainage systems have greatly increased the rate of  $L_o$ . Where backswamps may have been inundated for say 100 days under natural hydraulic conditions, the installation of floodgated drainage systems has resulted in excess water being removed from backswamps in less than one week. Since drainage does not alter P or  $E_t$  (assuming that crop vigour approximates native vegetation water use) but greatly increases  $L_o$ , a net increase in the water discharged from the system occurs. This results in a lowering of the watertable below its natural position. When the watertable is lowered below the level of sulphidic sediments, pyrite is oxidised, thereby acidifying the unsaturated soil layers above the watertable. Acid is subsequently discharged via the efficient drainage system by removing shallow groundwater directly to the drains and by the removal of excess surface water on filling of the acidified storage component of the soil profile during subsequent flooding.

As suggested above, management of subsurface hydrology at the sub-catchment scale is the key to the sustainable management of acid-sulphate soils. This paper demonstrates the relationships between the operation of deep flood mitigation drains, the elevation of groundwater levels in coastal lowlands and the generation of acidic oxidation products caused by the exposure of acid sulphate soil layers to oxygen using data from a field study site located near Berry on the NSW South Coast. The Simulation Model for Acid Sulphate Soils (SMASS) is used to evaluate the effectiveness of different groundwater regimes on the generation of acidic products from the oxidation of pyrite in the acid sulphate soils.

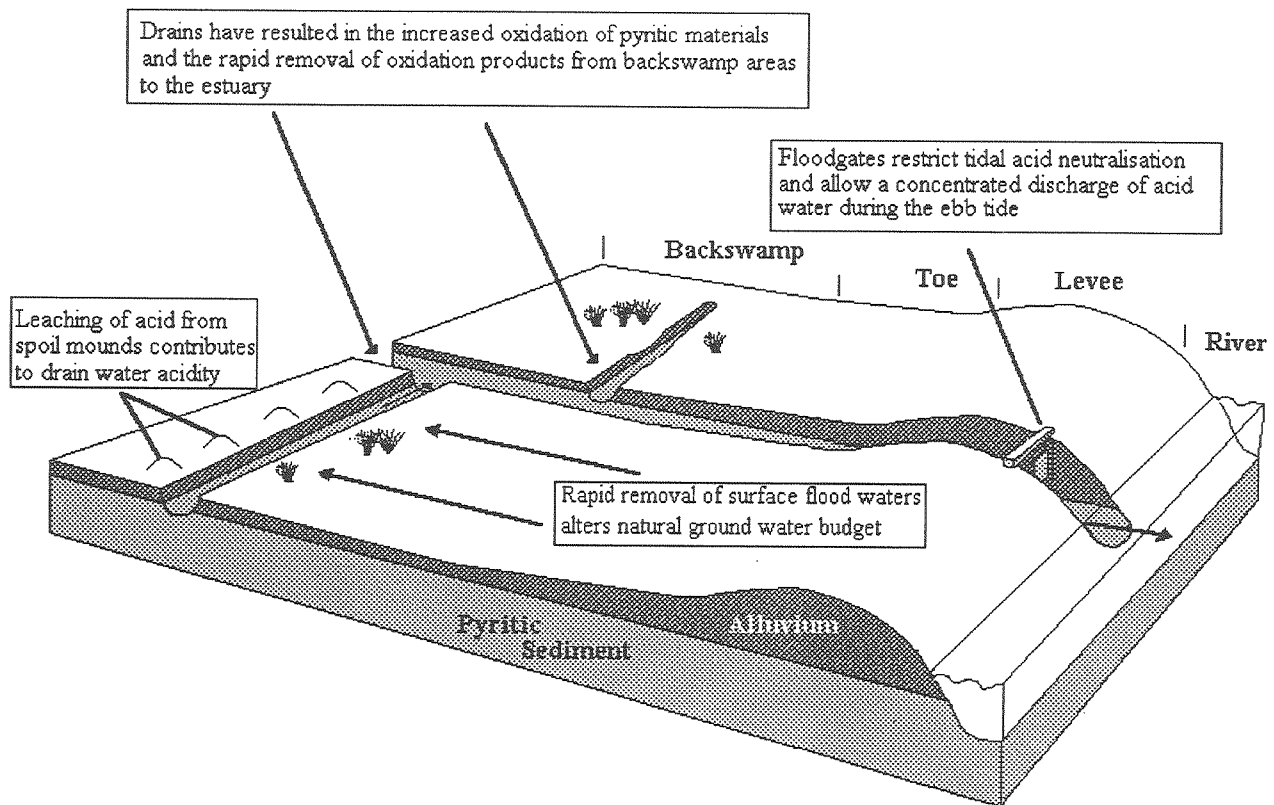


Figure 1 A typical coastal drainage system [from Naylor *et al.* (1995)].

## 2 MATERIALS AND METHODS

### 2.1 STUDY SITE

The study site is a small sub-catchment of approximately 120ha that has been extensively drained for agricultural and flood mitigation purposes. The site is adjacent to the township of Berry (34°S, 150°E) on the South Coast of New South Wales, Australia. A high density drainage network was constructed across the site in the late 1960's for flood control and surface drainage purposes. The drains discharge into Broughton Creek, a tributary of the Shoalhaven River. The two major flood mitigation drains are approximately 3.5m deep and 8m wide and discharge through a flood gate control structure which limits ingress of brackish estuarine water into the drainage system at high tide. The site is typical of coastal floodplains in New South Wales with the maximum elevation of 4m relative to the Australian Height Datum (AHD) and the lowest elevation <1m AHD. Sulphidic sediments formed during the Holocene period have been covered with shallow layers of alluvium approximately 1.3-1.4m deep. Piezometers located at a distances of 1, 10, 20, 50, 90 and 150m from the drains have been installed in eleven transects across the site to measure changes in the groundwater surface and associated changes in groundwater chemistry. Groundwater elevation was measured manually on a fortnightly basis.

### 2.2 RAINFALL

A weather station was installed at the site during 1997 to monitor climatic conditions. The average annual rainfall at the site is 1416mm year<sup>-1</sup>. Rainfall is not strongly seasonal though is slightly summer dominated. Mean pan evaporation peaks in late summer at 87mm month<sup>-1</sup> with corresponding winter minimum of 41mm month<sup>-1</sup>. However, during 1997-98 the site was influenced by both flood and drought conditions.

### 2.3 WATER QUALITY SAMPLING AND TESTING

Water quality monitoring of both surface and groundwater has taken place at this site since 1993. Regular spot measurements of pH and electrical conductivity have been made in the piezometers, drainage network and receiving

waters. In addition, water samples for laboratory analysis were collected from drains and piezometers at monthly intervals. pH and electrical conductivity were measured in the field using an Horiba D-24 probe that was calibrated prior to each monitoring period. Laboratory samples were immediately chilled upon collected then stored at 4°C until testing occurred. Acidification of samples was not required due to the low pH of the samples. Anions were measured using an atomic adsorption spectrometer and cations were measured using an ion chromatography.

## 2.4 SOIL PROPERTIES

### 2.4.1 SOIL PHYSICAL PARAMETERS

Cores of intact soil were collected from 5 locations across the study site. Sampling locations were selectively chosen across the site in order to establish soil physical characteristics both close to and further away from drains. Samples were collected at depths of 0.3, 0.6, 0.9, 1.2 and 1.5m from the ground surface. A backhoe pit was carefully excavated at each sampling location until the correct depth was obtained. An undisturbed bench was prepared inside the pit for collection of undisturbed samples. A thin walled brass core 100mm diameter and 70mm high was rapidly hit by guided drop hammer into the prepared bench for later laboratory determination of saturated hydraulic conductivity, dry bulk density and porosity. At each location and depth, 4 cores were collected in the vertical plane and 2 cores in the horizontal plane. Undisturbed cores 50mm diameter and 40mm high were also collected in the vertical plane for determination of the moisture characteristic curve. All cores were carefully excavated from the bench by hand and immediately wrapped in cling wrap and plastic bags to minimise moisture loss and to exclude air from the sample to prevent pyrite oxidation. Samples were stored at 4°C until laboratory testing was carried out. Saturated hydraulic conductivity was determined using the falling head method for 150 samples collected from 5 locations across the site, 5 depths within the soil profile and 2 orientations (horizontal and vertical). Measurements for determination of saturated moisture content, dry bulk density and porosity were also carried out. Soil moisture retention curves were determined using a high pressure extractor vessel and 15 bar porous ceramic plate. A 7 point moisture retention curve was determined by progressively applying vessel pressures of 10, 30, 60, 100, 330, 600 and 1000 kPa to the soil. After equilibrium was achieved at each pressure, the samples were carefully removed from the ceramic plate and weighed. Samples were then placed back onto the ceramic plate for application of the next pressure. After equilibrium was achieved at 1000 kPa, samples were weighed and oven dried at 105°C for 24 hours for determination of volumetric moisture content at each pressure. The unsaturated hydraulic conductivity function for these soils was determined using the saturated hydraulic conductivity and moisture characteristic data as input to the RETC code (van Genuchten *et al.*, 1991) which calculates the van Genuchten (1980) parameters.

### 2.4.2 SOIL CHEMICAL PARAMETERS

Soil was collected from eight locations across the site. At each location, samples were collected in 0.1m increments to a depth of 1.5m. The samples were collected by pushing a 60mm hollow steel tube into the soil to a depth of 1.0m using the NSW Agriculture Proline drill rig. This tube was extracted from the soil and the intact core divided into 0.1m increments, labelled and secured in a plastic bag. The additional 0.5m was sampled using a gouge auger attached to the Proline drill rig. Soil samples were divided and stored below 4°C for a few days until they could be dried at approximately 85°C. After drying the soil was ground and passed through a 2mm sieve. This soil was used for the determination of the pyrite concentration, pyrite size distribution, cation exchange capacity and organic matter content.

Pyrite content of the acid sulphate soil was determined using the POCAS technique (Ahern *et al.*, 1996). The pyrite size distribution was determined using electron microscopy. The cation exchange capacity was measured using the unbuffered BaCl<sub>2</sub> method.

## 2.5 SIMULATION MODEL FOR ACID SULPHATE SOIL (SMASS)

The computer model SMASS is described by Bronswijk and Groenenberg (1993) and Bronswijk *et al.* (1993). SMASS computes water movement and solute transport, pyrite oxidation and chemical reactions in a one-dimensional, vertical acid sulphate soils profile. The model consists of submodels for water transport, solute transport, chemical processes, oxygen transport and pyrite oxidation.

First the vertical water transport in the soil profile is computed within the water transport submodel, depending on the initial and boundary conditions. This submodel is based on the SWATRE model (Belmans *et al.* 1983) and yields the volumetric water content (and by difference volumetric air filled porosity) profile in the soil. From the air content profile, oxygen diffusion coefficients are calculated. Oxygen diffusion and oxygen consumption from pyrite and organic matter oxidation determine the oxygen concentration profile in the soil. The rate of pyrite oxidation at a given depth is then calculated depending on the oxygen concentration at that depth. The amount of pyrite oxidised at that

depth given the amounts of  $H^+$ ,  $SO_4^{2-}$  and  $Fe^{3+}$  released into the soil solution at that depth. The remaining amount of pyrite left is then used for calculations in the next time step. The solute transport submodel computes solute fluxes between soil layers depending on water fluxes. SMASS has been rigorously calibrated for numerous sites in South East Asia and Europe.

### 3 RESULTS AND DISCUSSION

#### 3.1 SOIL CHEMICAL PROPERTIES

The chemical properties of the soil confirm the presence of acid sulphate soils and also indicate that considerable oxidation of pyrite has occurred throughout the study area. The NSW Acid Sulphate Soils Management Advisory Committee (1998) suggests that where the concentration of pyrite is in excess of 0.1% oxidisable sulfur for clayey potential acid sulphate soils, then a risk to the environment may develop where these soils are disturbed. Figure 3 shows the concentration and variability of pyrite down a soil profile sampled at the Berry site, which indicates that the pyrite layer starts at about 1.3m below the ground surface.

The average pyrite concentration in the potential acid sulphate soil is about 2.2%, however this varies both spatially and with depth. The formation and concentration of pyrite is dependant on the presence of organic matter. Often pyrite is concentrated in relics of root channels or other vegetative remnants which are unevenly distributed through the soil profile. The pyrite concentration at this site is typical of potential acid sulphate soils along the southern parts of the east coast of Australia and suggests that a considerable risk is present if these soils are disturbed and pyrite oxidation occurs.

The soil pH profile described in Figure 3 shows that the whole soil profile is strongly acidic. The pH quickly grades downwards from a relative high at the surface (pH 5.0) to 3.5 at the bottom of the surface alluvial layer (about 0.5m depth). The soil pH declines further to a minimum of 2.8 at the transition between the non-acid sulphate soil and the oxidising zone at about 1.3m depth. The zone directly above the oxidising layer is characterised by pH of 3 and the presence of jarosite mottles and iron coatings on the faces of structural elements in the soil. At deeper depths pH increases with increasing distance away from the oxidation front.

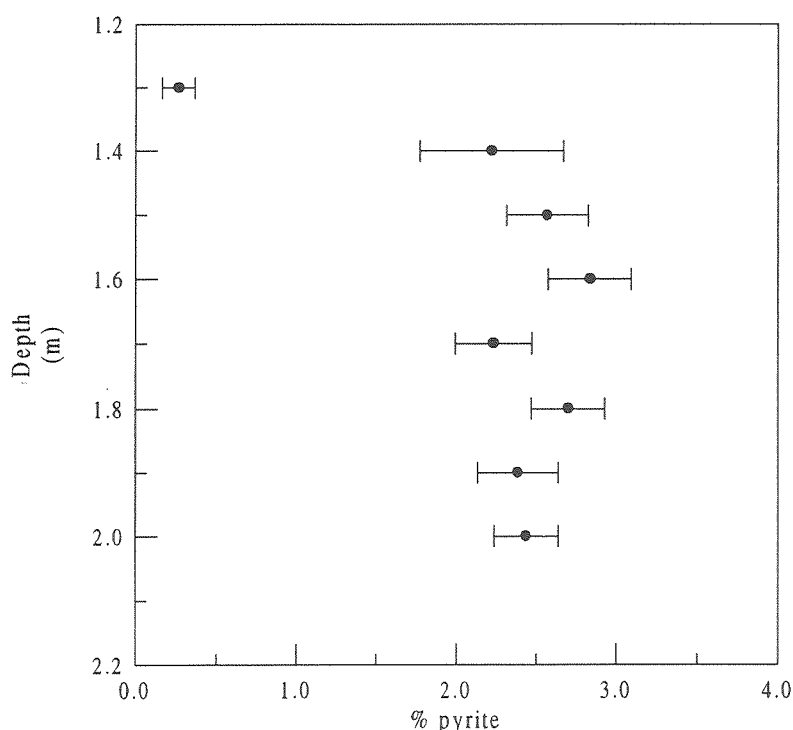


Figure 2 Concentration and variability of pyrite.

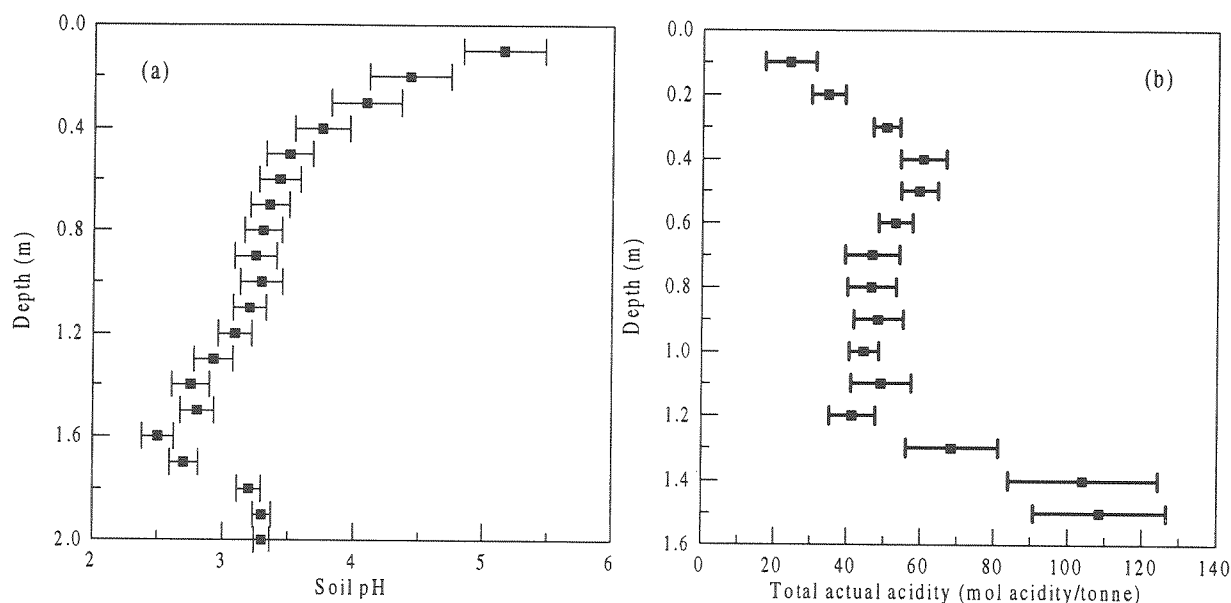


Figure 3 (a) soil pH and (b) total actual acidity.

A considerable store of acidity was also identified in the soil profile. Conversion of the total actual acidity data to a volumetric basis for the first 1.5m of the profile indicates that  $50 \text{ mol acidity m}^{-2}$  (or  $25 \text{ tonnes H}_2\text{SO}_4 \text{ ha}^{-1}$ ) is available in readily soluble form for redistribution within the profile and transport to the drainage system. This indicates that even if no further acid is generated in the pyritic zone in the future, the soil will likely remain strongly acid until the existing store of acidity is either leached from the soil or neutralised.

The rate of pyrite oxidation is also influenced by the particle size distribution of the pyrite. Bush and Sullivan (1996) have reported singular cubic pyrite crystals smaller than  $1 \mu\text{m}$  diameter to framboidal clusters of pyrite in excess of  $200 \mu\text{m}$  diameter. Many pyrite oxidation numerical models, including SMASS, simulate the oxidation of pyrite using a shrinking spherical core regime. As the core shrinks, the surface to volume ratio of the pyrite crystal increases thereby increasing the rate of oxidation of the pyrite. Figure 4 shows the size distribution of pyrite from the potential acid sulphate soil sampled at the Berry site from a depth of 1.5m.

The mean pyrite diameter is  $1.02 \mu\text{m}$ . All the pyrite crystals are relatively small and suggest that they exist as individual crystals rather than in framboids. The small diameter of the pyrite crystals suggests that pyrite oxidation may occur at a rapid rate once oxidising conditions are established.

The constitution of the cation exchange capacity (CEC) also indicates that severe acidification has occurred. The CEC and percentage base saturation are given in Table 2. The cation exchange capacity is dominated by exchangeable aluminium and hydrogen. Both these cations are acidic and are considered to be toxic to pasture species in concentrations above 10% of the cation exchange capacity of the soil or where the base saturation fall below 90%. The profile exhibits a base saturation ranging from 22.89% in clayey potential acid sulphate soil to 13.23% in a relatively sandy horizon at 0.9 m depth. The low base saturations indicate that basic cations have been lost from the soil thereby lowering its ability to buffer acidic conditions. The relatively high base saturation at the surface is due to the incorporation of lime (as shown by the elevated Ca measurement) by the land managers and higher levels of organic matter that comprise part of the exchange complex.



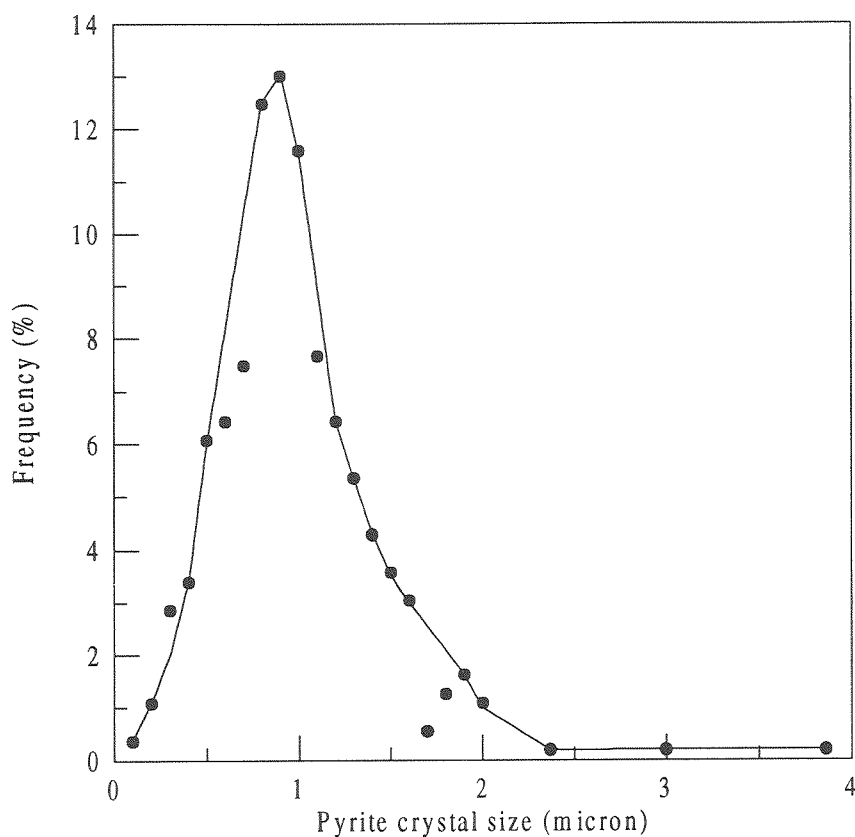


Figure 4 Pyrite size distribution.

Depth (m)	Na	K	Ca	Mg	Al	H	CEC cmol kg <sup>-1</sup>	base saturation (%)
0.3	0.3	0.3	2.32	0.66	10.65	3.48	17.72	20.27
0.6	0.2	0.3	0.68	0.41	7.97	2.00	11.52	13.46
0.9	0.2	0.2	0.62	0.50	7.66	2.28	11.46	13.23
1.2	0.3	0.1	0.74	0.93	6.96	2.28	11.33	18.44
1.5	0.7	0.3	1.58	3.42	10.77	9.24	25.95	22.89

Table 2 Cation exchange composition and base saturation.

### 3.2 SOIL PHYSICAL PROPERTIES

Soil physical parameters determined from saturated hydraulic conductivity and moisture characteristic data are given in Table 3.

Depth (m)	$W_r$	$W_s$	$\alpha$ (m <sup>-1</sup> )	$n$	$k_v$ (m day <sup>-1</sup> )	$k_v/k_n$	$\rho_b$ (kg m <sup>-3</sup> )
0.3	0.05	0.49	0.281	1.30	3.95	1.06	650
0.6	0.02	0.35	0.242	1.15	3.84	1.02	1110
0.9	0.05	0.34	2.917	1.18	1.68	2.15	1050
1.2	0.04	0.50	0.2247	1.29	2.08	2.36	950
1.5	0.06	0.49	0.4737	1.11	2.02	12.7	1030

Table 3 Soil physical properties.

where  $W_r$  and  $W_s$  are residual and saturated volumetric moisture contents,  $\alpha$  and  $n$  are shape parameters from the van Genuchten (1980) equation,  $k_s$  is the saturated hydraulic conductivity in the vertical plane ( $k_v$ ) and in the horizontal plane ( $k_h$ ),  $\rho_b$  is dry bulk density.

The  $k_v$  is very high throughout the soil profile.  $k_h$  was influenced by large, continuous macropore channels that were observed at all depths in the soil profile. The  $k_v$  of the potential acid sulphate soil layer (depth 1.5m) at this site is unusually high when compared to other areas (White *et al.* 1997). However,  $k_h$  of the potential acid sulphate soil is typically low due to the massive structure that exists between vertical macropores in the soil matrix and the clayey nature of the potential acid sulphate soil. This leads to high  $k_v/k_h$  ratios for the potential acid sulphate soil layer. The ratio of hydraulic conductivity in the vertical plane to the horizontal plane ( $k_v/k_h$ ) in Table 3 shows that lateral groundwater flow becomes progressively slower with increasing depth. In the potential acid sulphate soil at 1.5m depth, the horizontal hydraulic conductivity is only 0.16m day<sup>-1</sup>. This indicates that lateral removal of groundwater to the drains will become progressively slower as the elevation of the groundwater falls.

In many areas, potential acid sulphate soil  $W_r$  between 0.8-1.2,  $\rho_b$  of 0.4-0.6 and the consistency of a gel (White *et al.* 1997) which in turn reduces  $k_{sat}$  to almost zero. The potential acid sulphate soils at Berry appear to have undergone a consolidation phase where water has been permanently removed from the soil. Consolidation and the creation of macropore channels by roots has given rise to a highly permeable soil structure which is readily able to transport oxygen from the soil surface to the pyritic layers when groundwater falls below the depth of the acid sulphate soil.

$\alpha$  and  $n$  are parameters that describe the shape of the moisture characteristic and unsaturated hydraulic conductivity curves.  $\alpha$  is approximately the reciprocal of the air entry value of the soil.  $\alpha$  values shown in Table 3 indicate that the largest pores drain at a soil water suction of 35 kPa in the surface soil and at only 21 kPa in the potential acid sulphate soil. These low air entry values indicate that the soil structure comprises of large continuous macropores which readily conduct air when the soil initially becomes unsaturated. The unimpeded transport of oxygen through this easily drained pore space gives rise to the rapid oxidation of pyrite in the acid sulphate soil soon after the groundwater has fallen below the depth of the acid sulphate soil.

### 3.3 GROUNDWATER HYDROLOGY

Groundwater levels have varied considerably during the study period and have largely been determined by groundwater flow to the drains, rainfall and evapotranspiration. A series of groundwater profiles from transect I is shown in Figure 5 to illustrate the influence of these factors for the 350 day period starting 18 July, 1997. The profile at day 28 shows a typical drainage profile where the level of water in the drain is below the groundwater level in the surrounding catchment to cause a hydraulic gradient to exist. The hydraulic gradient causes groundwater to flow towards the drain and discharge to the drain through seepage faces in the drain walls. Seepage from the field into the drain continues whilst the hydraulic gradient is in that direction. Prolonged seepage in the absence of groundwater recharge from either rainfall or upland groundwater movement will result in a relatively flat groundwater profile where the water level in the drain is in equilibrium with the surrounding groundwater level. This equilibrium was achieved around day 179. The groundwater elevation at piezometers I10 and I90 are shown in Figure 6 along with the rainfall and evapotranspiration record for the study period.

Where evapotranspiration exceeds the groundwater recharge rate, groundwater may be removed from shallow aquifers. From Figure 5 at day 238, it is apparent that the groundwater level falls progressively more as the distance from the drain increases. This is caused by evapotranspiration removing water from the soil profile. Figure 6 demonstrates that evapotranspiration has had a more substantial impact on the groundwater level at I90 than I10. The groundwater levels at I10 has been maintained by the constant water level (low tide level) in the drains. Seepage has occurred through the drain walls, though the resupply rate from the drains is not sufficiently rapid to transport water laterally through the lower soil layers to influence groundwater levels further away from the drains. As described previously, the saturated hydraulic conductivity of the acid sulphate soil layer is very slow in the horizontal plane, thereby limiting recharge of groundwater from the drains.

### 3.4 GROUNDWATER HYDROLOGY-CHEMISTRY

The piezometer transect data indicate that the groundwater levels fell substantially below the elevation of the acid sulphate soil layer during the summer of 1997-98. Low groundwater levels enable oxygen to diffuse to the acid sulphate soils enabling oxidation of pyrite and acid generation to occur. The relationship between groundwater elevation, the depth of the acid sulphate soil layer and the pH of the groundwater is shown in Figure 7(a,b) for piezometers I10 and I90.

Figure 7 shows a number of interesting features relating the groundwater hydrology and concentration of acidity in the groundwater. Initially the groundwater elevation is substantially above the potential acid sulphate soil layer. The oxidation of pyrite and the generation of new acidic products is minimal at this groundwater elevation. However, the pH of the groundwater is very low (pH 3-4). The low pH is due to previously generated acid in the oxidation zone being dissolved in the rising groundwater. This reserve of acid within the groundwater is then transported towards the drains and discharged through seepage face causing acidification of the drain water (typically pH 3-5).

The pH of the groundwater rises during periods of high rainfall where the soil profile becomes fully saturated and runoff occurs. At days 40 and 55, in excess of 85mm of rainfall fell causing flooding in the catchment. Acid stored within the soil profile was leached to the surface and removed from the site with the flood waters reducing the store of acidity in the soil profile. Higher pH values remained in the groundwater until further acid was generated in the acid sulphate soil layer. The groundwater pH remained high (pH 5-6.5) throughout the summer period even as the groundwater level fell below the elevation of the acid sulphate soil layer. During this time, acid was being generated in the acid sulphate soil layers above the groundwater table. However this store of acid was being held under suction in the soil pore water at its place of origin. The relatively small amount of acidity already dissolved in the groundwater was buffered by calcium carbonate (shell) deposits and the higher percentage of exchangeable bases within the cation exchange complex present at depth in the acid sulphate soil layer.

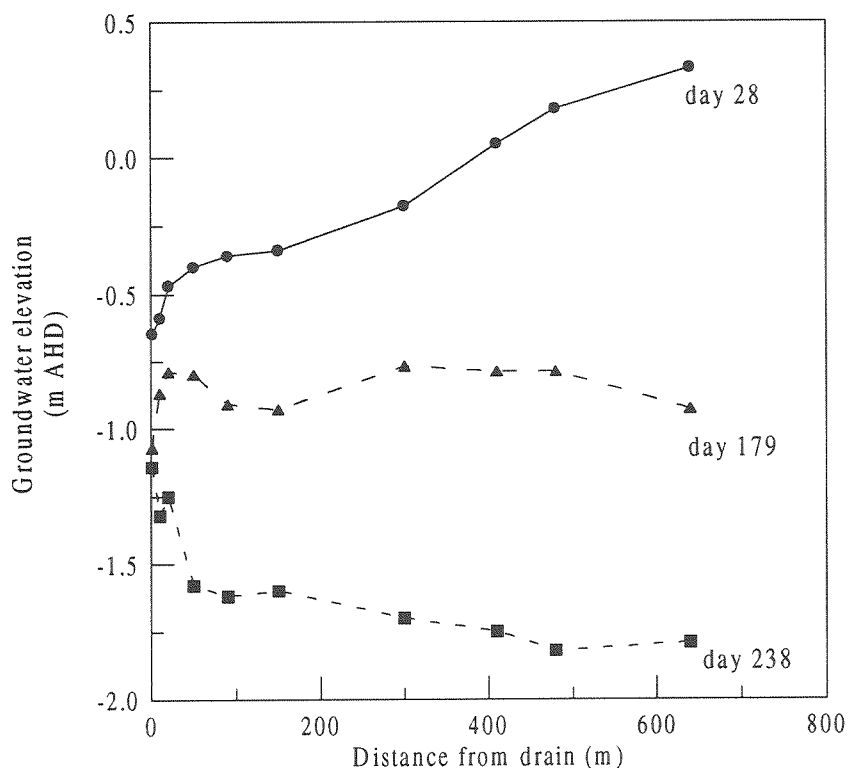


Figure 5 Groundwater profiles at transect I.

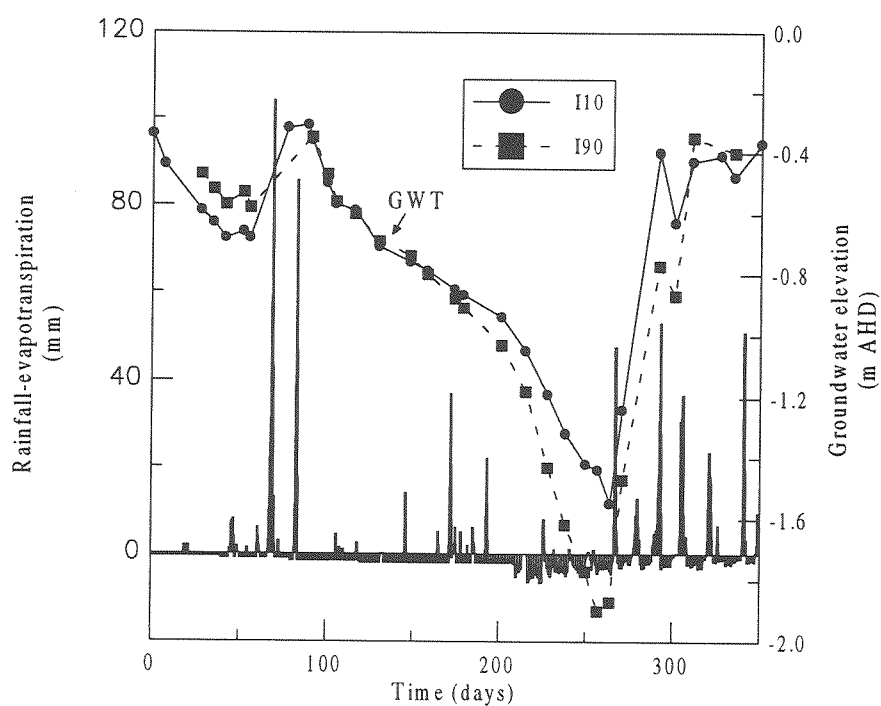


Figure 6 Groundwater elevation at I10 and I90 with rainfall - evapotranspiration.

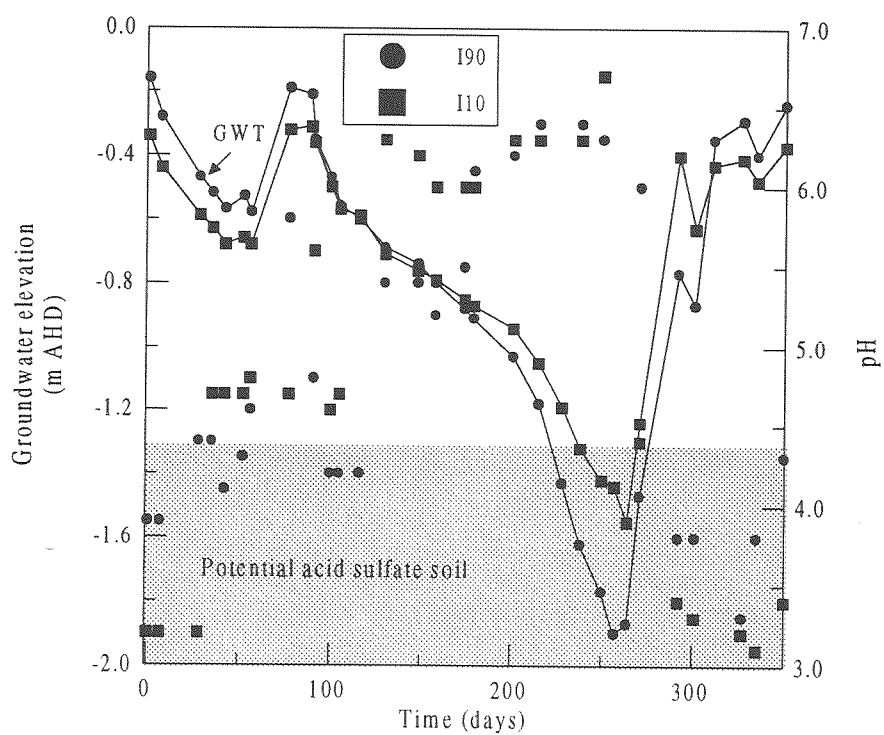


Figure 7 Temporal variability of groundwater elevation and pH

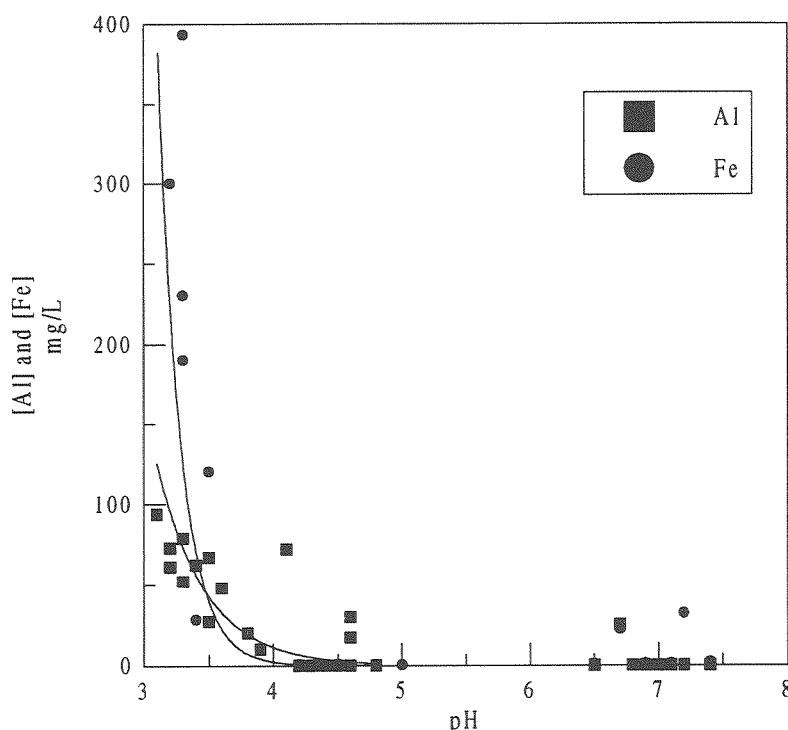


Figure 8 Variation of  $[Al^{3+}]$  and  $[Fe^{3+}]$  with pH

On breaking of the drought period, the groundwater rose through the oxidised pyritic layer mobilising the acid that had been generated during the period of low groundwater elevation. At this time the groundwater become strongly acidic (pH 3.1). Groundwater sampled from piezometers in transects A-E had a pH between 1.9 and 2.3. Low groundwater pH values have remained since the drought breaking rains as a result of the very large store of acid generated during the period of low groundwater elevation, and the absence of flooding events that may remove some of the acidity dissolved in the groundwater.

### 3.5 GROUNDWATER CHEMISTRY

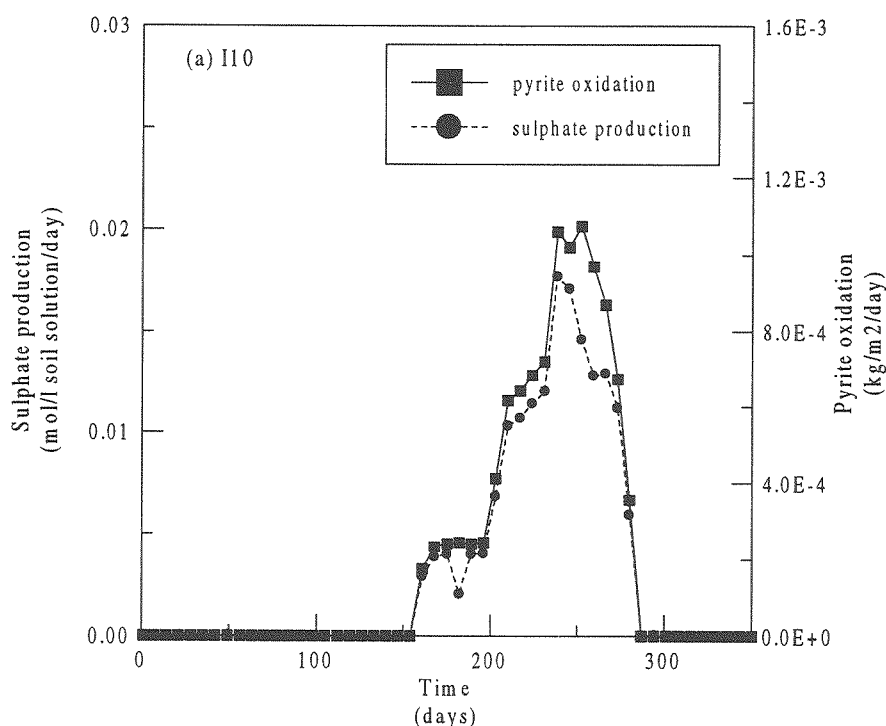
The concentration of soluble Al and Fe is strongly dependant on pH. Figure 8 shows that  $[Al^{3+}]$  and  $[Fe^{3+}]$  are logarithmically proportional to pH. Sammut *et al.* (1996) described similar data for waters sampled in northern New South Wales. The concentration of soluble Al and Fe increases as pH of the groundwater falls below pH ~5.5. Sammut *et al.* (1995) show that  $H^+$  and dissolved species of Al play an important role in the death or injury of aquatic organisms. Acid sulphate soil management strategies should aim to decrease the acidity of ground and drain water to pH >5.5 to minimise the risks of environmental degradation. Sammut *et al.* (1996) observed that iron is removed as it transfers from groundwater to the drains. They hypothesise that as groundwater enters the drains iron may floc from the water column. Iron flocs can form in conditions where pH >2.7, though Sammut *et al.* (1996) describe that under low flow conditions, iron flocs are not usually present at pH <4. The concentration of  $Fe^{2+}$  measured in the drains is many orders of magnitude less than that found in the groundwater. Large amount of iron flocs and deposits of black iron monosulphides on the base of the drains have been observed at the study site and may account for the difference in dissolved iron concentrations measured between the groundwater and drains.

### 3.6 SIMULATION MODEL FOR ACID SULPHATE SOILS (SMASS)

Laboratory measurements and field data were used to initialise SMASS for the simulation of the existing drained conditions at the site. A summary of the data requirements for SMASS is described in Table 4. This data is expensive and time consuming to collect and is not generally available for sites containing acid sulphate soils in Australia. Given the large data requirement and the general user-unfriendliness of the model, SMASS is predominantly a research tool that can be used to develop simplified management rules for more general application.

Simulation was carried out for one location 10m from the drain (I10) and another location 90m from the drain (I90) to assess the influence of the drain on the generation of pyrite oxidation products. Figure 10 (a,b) shows the amount of sulphate produced from the oxidation of pyrite and the rate at which pyrite oxidation occurs predicted by SMASS.

Figure 9 also shows that pyrite oxidation and the subsequent generation of sulphate corresponded to the fall of the groundwater below the acid sulphate soil. During the period where groundwater level was lower than the acid sulphate soil layer, 0.077 and 0.080 kg pyrite m<sup>-2</sup> oxidised at I10 and I90 respectively, which generated 1.29 and 1.33 mol SO<sub>4</sub><sup>2-</sup> m<sup>-2</sup> (or 1.29 and 1.33 tonnes H<sub>2</sub>SO<sub>4</sub> ha<sup>-1</sup>). At I10, the oxidation of pyrite commenced at day 161 whereas at I90 pyrite oxidation started at day 189. The earlier start of pyrite oxidation at I10 was caused by the drawdown effect of the drain rapidly removing groundwater from the soil by seepage in the volume of soil close to the drain. Given the low lateral hydraulic conductivity of the acid sulphate soil, it took another 28 days for sufficient drainage to occur until the groundwater fell below the acid sulphate soil layer at I90. However, the fall of groundwater below the acid sulphate soil layer at I10 was moderated by the maintenance of water at about -1.45m AHD in the drains. Seepage from the drains recharged the shallow aquifer at I10 thereby minimising the lowering of the groundwater by evapotranspiration. At I90, recharge from the drains was not sufficient to overcome evapotranspiration which caused the groundwater elevation to fall to -1.8m AHD.



SMASS input data	Method
Groundwater table levels	Manual piezometer measurement
Evapotranspiration	Automatic weather station
Soil moisture characteristic curve	Pressure plate apparatus
Dry bulk density	Gravimetric determination using soil cores
Average aggregate radius	Soil profile description
Saturated hydraulic conductivity	Falling head technique
Pyrite concentration	POCAS
Organic matter content	Leco C, N, S
Mean pyrite diameter	Electron microscope
Soil water chemistry (Na, Mg, Ca, K, SO <sub>4</sub> , Fe, Cl, HCO <sub>3</sub> , pH, EC, Eh)	Probes, Ion Chromatography, Atomic Adsorption Spectrography
Cation Exchange Capacity	unbuffered BaCl <sub>2</sub> method
Oxygen diffusion coefficient	literature
Various constants	literature

Table 4 Data requirements for SMASS

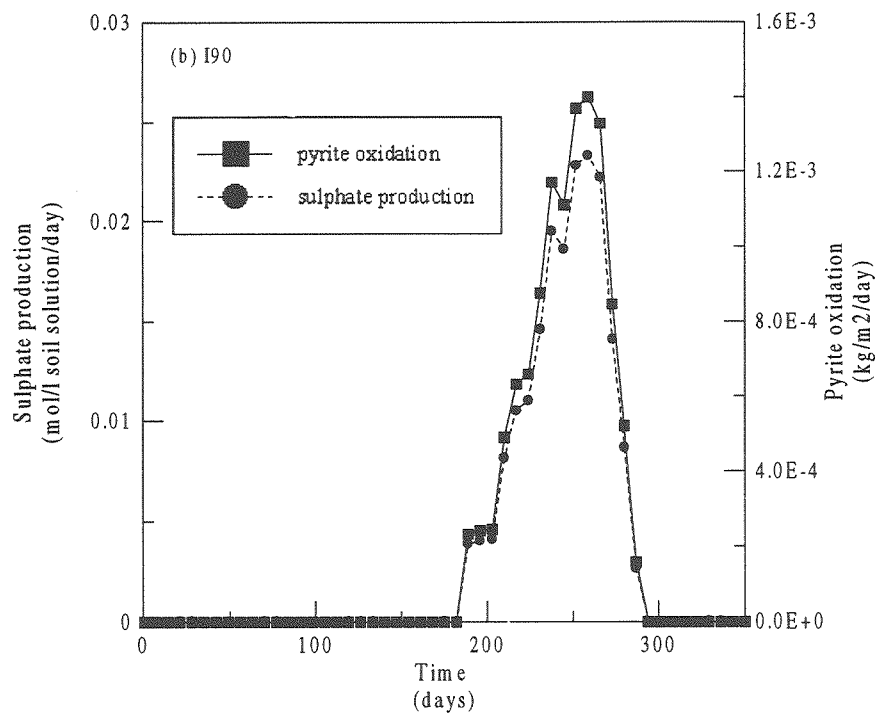


Figure 9 SMASS predicted sulphate production and pyrite oxidation for I10 and I90

The elevation of the groundwater has a significant impact on the acid generation rate. As a greater depth of acid sulphate soil becomes unsaturated and is exposed to oxygen, a greater quantity of pyrite within the soil is oxidised. SMASS simulation output from sites I1, I10, I90, F150 and D150 was used to determine a general relationship between the groundwater elevation and the acid generation rate from the oxidation of pyrite in the acid sulphate soil layer. Figure 10 shows the groundwater elevation - pyrite oxidation rate relationship.

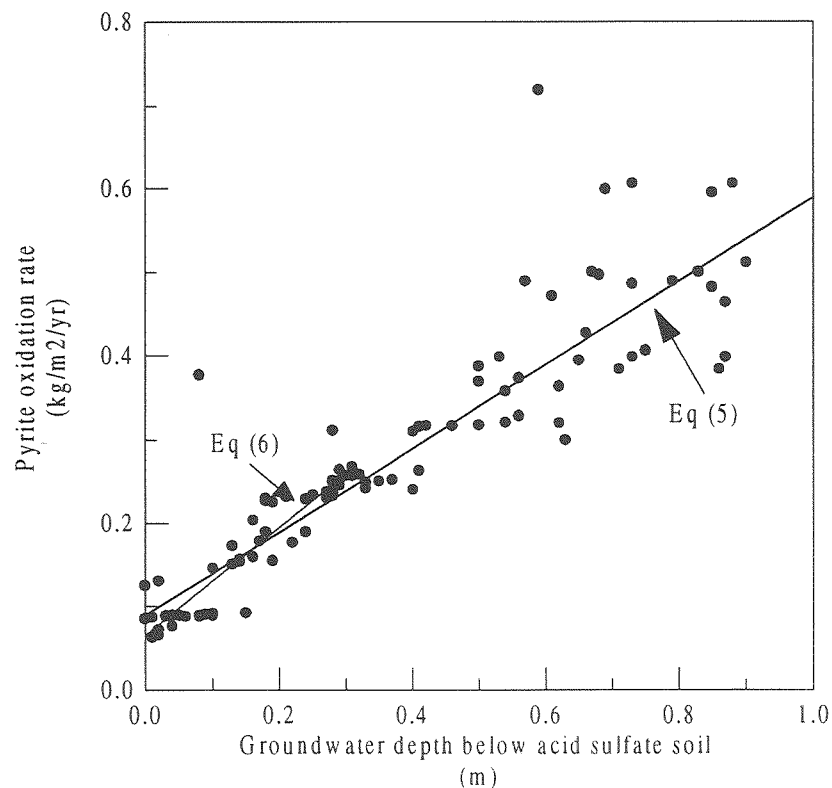


Figure 10 Pyrite oxidation rate determined by groundwater elevation

As the groundwater level falls the rate of pyrite oxidation increases. Linear regression analysis gives:

$$\text{POR} = 0.50\text{GWL} + 0.089 \quad r^2=0.80 \quad (5)$$

where POR is the pyrite oxidation rate ( $\text{kg m}^{-2} \text{yr}^{-1}$ ) and GWL is the difference between the upper surface of the acid sulphate soil layer and the groundwater elevation (m). Significant scatter is observed in the POR data where GWL exceeds 0.4m. This may be explained by increasing non-linearity of the pyrite oxidation solution using the shrinking core numerical scheme where the size of pyrite crystals being simulated varies considerably throughout the oxidising part of the acid sulphate soil horizon. Given that Equation (5) is determined using GWL data measured during a severe drought, a more promising regression equation may be described if the GWL is restricted to less than 0.3m. Linear regression for GWL less than 0.3m gives:

$$\text{POR} = 0.65\text{GWL} + 0.065 \quad r^2=0.89 \quad (6)$$

Equation (6) resembles the groundwater regime similar to that described in Figure 6 for the groundwater profile at day 179, where drawdown of the groundwater surface is caused by the hydraulic gradient imposed by the flood mitigation drains.

Regression functions such as described in Equations (5) and (6) may prove valuable in developing and assessing remedial strategies for disturbed acid sulphate soil landscapes, particularly when the data requirements necessary to initialise SMASS are taken into consideration. The SMASS model and other similar pyrite oxidation numerical models that have been developed for the prediction of acid generation from pyritic mine tailings (eg. Wunderly *et al.*, 1996) are expensive in terms of their data requirements to initialise the model, in computational effort and operator experience to analyse the simulation output. Equations (5) and (6) could readily be incorporated into relatively simple models that predict groundwater elevations based on soil physical properties, the geometry of drains and climatic data to calculate the amount of acid generated at a site for specific groundwater management options.

## 4 MANAGEMENT OF ACID SULPHATE SOILS BY GROUNDWATER MANIPULATION

### 4.1 GROUNDWATER MANAGEMENT BY DRAIN WEIRS

In order to minimise the amount of acid generated in acid sulphate soils in a drained subcatchment, it is necessary to limit the exposure of pyrite in the soil to oxygen. Raising the groundwater table so that it is permanently above the pyritic layer reduces the diffusion of oxygen to the pyritic sediments thereby limiting the generation of acid.

The installation of weirs within the flood mitigation drains to elevate the water levels within the drains has been proposed as one method of elevating groundwater levels at the sub-catchment scale. In short, the current operation of floodgated drainage systems ensures that the level of water in the drains is at about the low tide level. In many instances, low tide level is well below the elevation of the acid sulphate soil layer in the surrounding catchment. Such a low drain water level gives rise to a hydraulic gradient where the shallow groundwater flows into the drain lowering the surrounding groundwater table. As groundwater drainage occurs, the acid sulphate soils become unsaturated giving rise to the entry of oxygen and subsequent generation of acid. Setting the elevation of weirs above the acid sulphate soil layer will reduce the hydraulic gradient caused by the drain. Under 'normal' climatic conditions, it is envisaged that elevated drain water levels will maintain groundwater levels above the acid sulphate soil horizon. In addition, as the hydraulic gradient from the groundwater to the drain will be reduced, the rate of discharge of the existing acidity in the soil to the drain will be slowed. The slower acid discharge rate may enable the natural buffering capacity of the receiving waters to neutralise the slow leakage of acidity.

Two adjustable weirs have been installed in the flood mitigation drains at the Berry site in 1998. The weirs raise the water level in the drains to 0.1 and 0.6m above the acid sulphate soil layer. The weirs were constructed by driving wooden poles approximately 3m into the invert of the drain then fixing marine ply boards to the poles to form the weir. The weirs were concreted into the sides of the drains then covered with rip-rap to prevent erosion of the drain edge. Fill was placed either side of the boards to ensure stability of the structure during flood events and to minimise leakage through the weir. A V notch weir was incorporated into the weir to measure the flow rate in the drain during low flows. A cross sectional diagram of the weir is given in Figure 11.



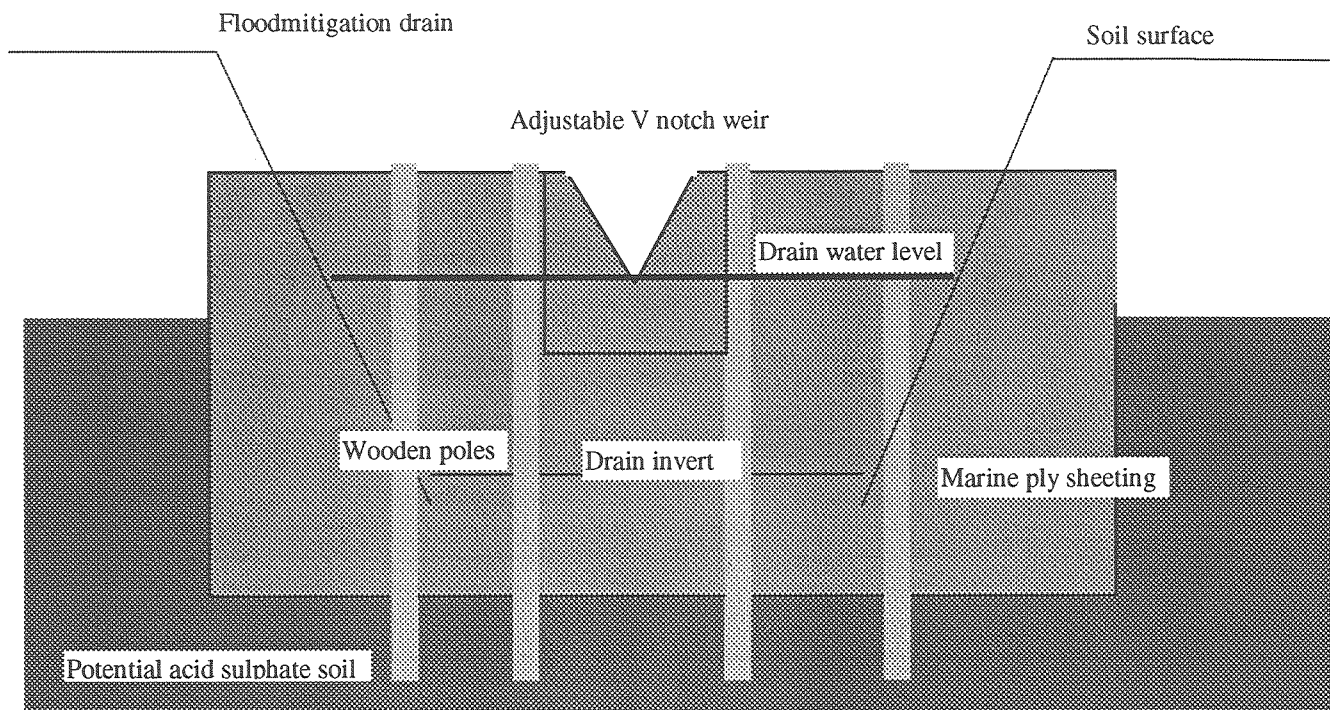


Figure 11 Adjustable weir for control of drain water level

A comprehensive monitoring program is underway to assess the effectiveness of raising the water level in the drains using weirs to minimise pyrite oxidation in the surrounding potential acid sulfate soil. Groundwater elevation, soil and groundwater chemistry and the chemistry of water discharged through the drainage system will be compared to the baseline conditions that existed prior to the installation of the weirs. Regular monitoring will continue until 2000 where a reassessment of the frequency and number of water quality parameters monitored will be reviewed.

#### 4.2 OTHER GROUNDWATER MANAGEMENT STRATEGIES

Increasing the water balance input to a site may elevate groundwater levels or keep upper soil layers sufficiently saturated to minimise the oxidation of pyrite. Examination of Equation (4) shows that the only strategy available to increase the input side of the water balance equation is by the implementation of irrigation. Unfortunately, the supply of secure sources of irrigation water is scarce in eastern Australia and the economic returns available to irrigated pasture are low, thereby limiting the implementation of this acid sulphate soil management strategy.

Filling existing deep flood mitigation drains that affect groundwater levels and replacing these with a high density network of broad, shallow drains that do not intersect the acid sulphate soil layer may also prove effective in minimising acid generation. Removal of the hydraulic gradient imposed by deep flood mitigation drains may result in the elevation of groundwater levels by reducing the lateral outflow component defined in Equation (4). This strategy has many potential benefits including better (or equivalent) flood protection, increased area available for pasture production and better drought protection for farmers. However, the cost of infilling existing deep drainage systems and constructing new, shallow drainage systems is expensive.

### 5 CONCLUSION

Deep flood mitigation drains lower the elevation of the surrounding groundwater below 'natural' conditions. Where the elevation of groundwater falls below the acid sulphate soil layer, oxidation of pyrite occurs leading to the generation of large quantities of sulfuric acid. Sulfuric acid can be stored in the soil profile and/or transported to drains which then discharges large volumes of low pH water to estuarine systems causing significant environmental and economic impacts.

Lowering of the groundwater at the Berry during the summer of 1997-98 caused approximately 1.3 tonnes  $\text{H}_2\text{SO}_4 \text{ ha}^{-1}$  to be generated from the oxidation of pyrite in the acid sulphate soil layer. After breaking of the drought, groundwater rose through the oxidised zone mobilising the stored acidity within the soil profile and caused acidification of the groundwater (pH 2-3).

Application of SMASS using soil physical and chemical data collected from the site in conjunction with measured groundwater elevation and climate data enabled a linear regression equation relating groundwater depth to the acid generation rate to be calculated. This regression equation may be used in conjunction with simple groundwater numerical models to assess the effectiveness of land management strategies in minimising the generation of acidic oxidation products in coastal landscapes containing acid sulphate soils.

Better management and manipulation of groundwater levels is the key for sustainable management of acid sulphate soils. The installation of weirs in flood mitigation drains to reduce the hydraulic gradient imposed by the drains has been implemented in an effort to elevate the groundwater elevation above the acid sulphate soil layer. Other strategies such as irrigation or filling existing drains and implementing shallow drainage systems that rapidly remove surface flood waters, but do not impact on groundwater elevations may also be effective in managing acid sulphate soils at the subcatchment scale.

## 6 ACKNOWLEDGEMENTS

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